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SILICON-CONTAINING MOIETIES AS ENHANCERS OF SEGMENT AND JUNCTION FLEXIBILITY IN HIGH-TEMPERATURE THERMOSETTING POLYMER NETWORKS

11 December 2012

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Outline

- Background / Motivation
  - Cyanate esters
  - Reasons for incorporating silicon into thermosetting resins
- Cyanate esters with Si substituted for C
  - Effect of Si Substitution on Crystal / Volumetric Properties
  - Effect of Si Substitution on Water Uptake
  - Effect of Si Substitution on Processing and Cure
- Cyanate esters containing siloxane segments

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AFRL Mission

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Cyanate Esters for Next-Generation Aerospace Systems

Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

Onset of Weight Loss:
> 400 °C with High Char Yield

Resin Viscosity Suitable for Filament Winding / RTM

Good Flame, Smoke, & Toxicity Characteristics

Compatible with Thermoplastic Tougheners and Nanoscale Reinforcements

Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

Cyanate Esters Around the Solar System

Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor

Fusion reactor, photo courtesy of Gerritse ((Wikimedia Commons)

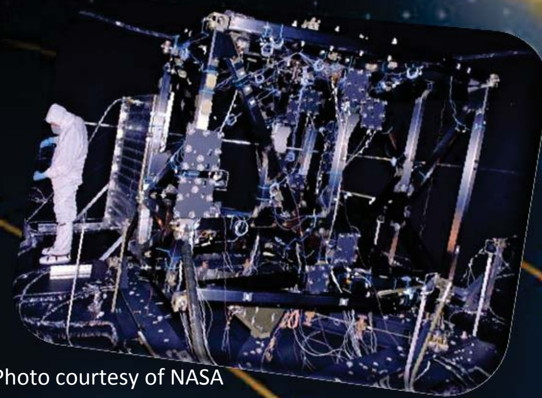


Photo courtesy of NASA

- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope

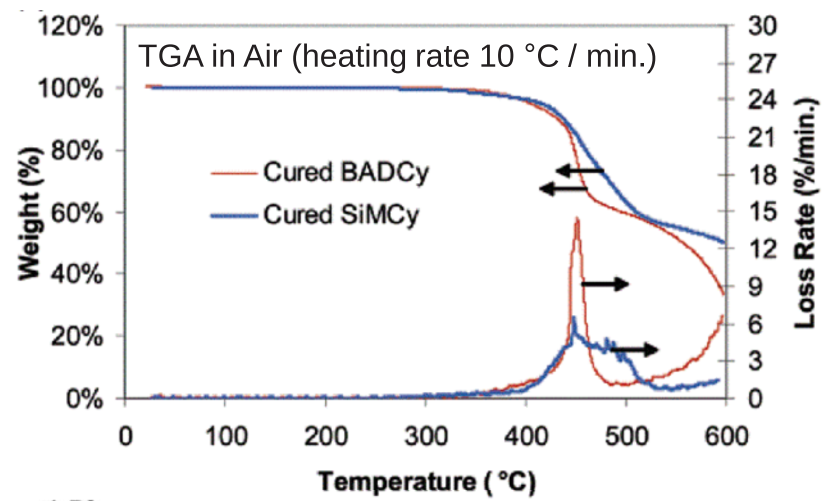
- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites

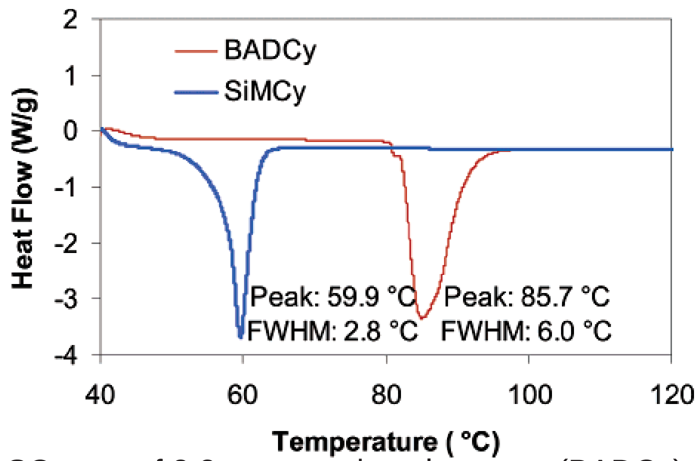
- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

Images: courtesy NASA (public release)

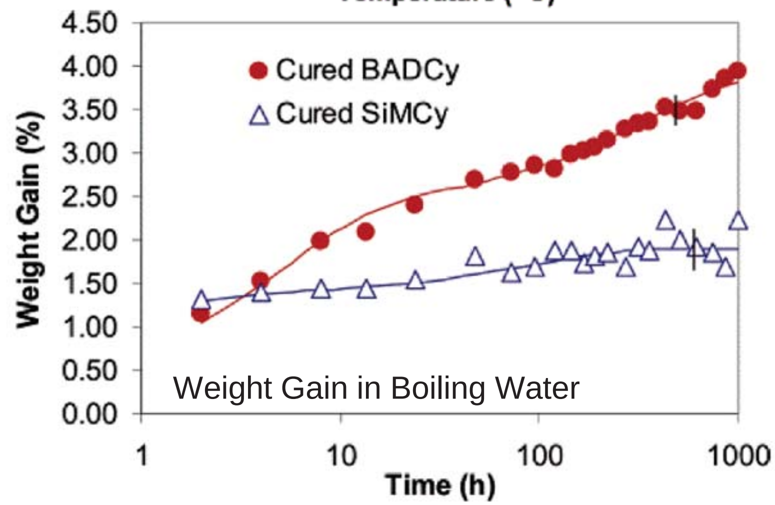
The Use of Si in Thermosetting Polymers

Silicon has mainly been used as a rigid reinforcement to promote improved mechanical and thermo-oxidative performance. Some examples of the use of silicon at a molecular level, in flexible rather than rigid form, are known (e.g. Wright et al., Polymer Preprints, 2004, 45(2), 294.



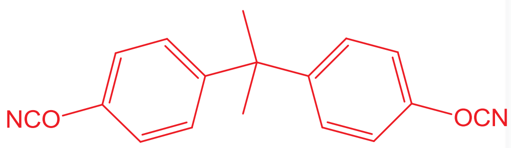


DSC scan of 2,2-cyanatophenylpropane (BADCy) and bis- (4-cyanatophenyl)dimethylsilane 3 (SiMCy) near the melting point.

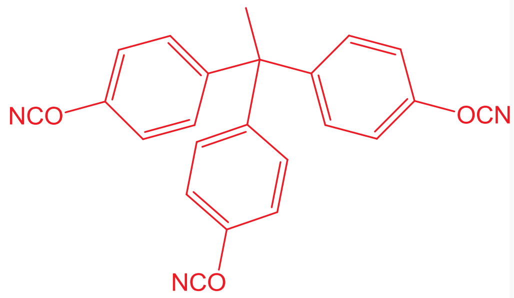


- In addition to the expected increase in short-term thermo-oxidative stability; the substitution of Si also results in lower melting temperatures and lower water uptake

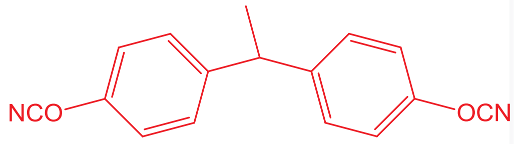
Si-Containing Cyanate Ester Monomers



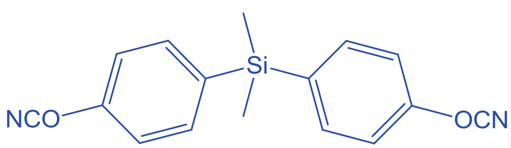
BADCy



ESR255



LECy

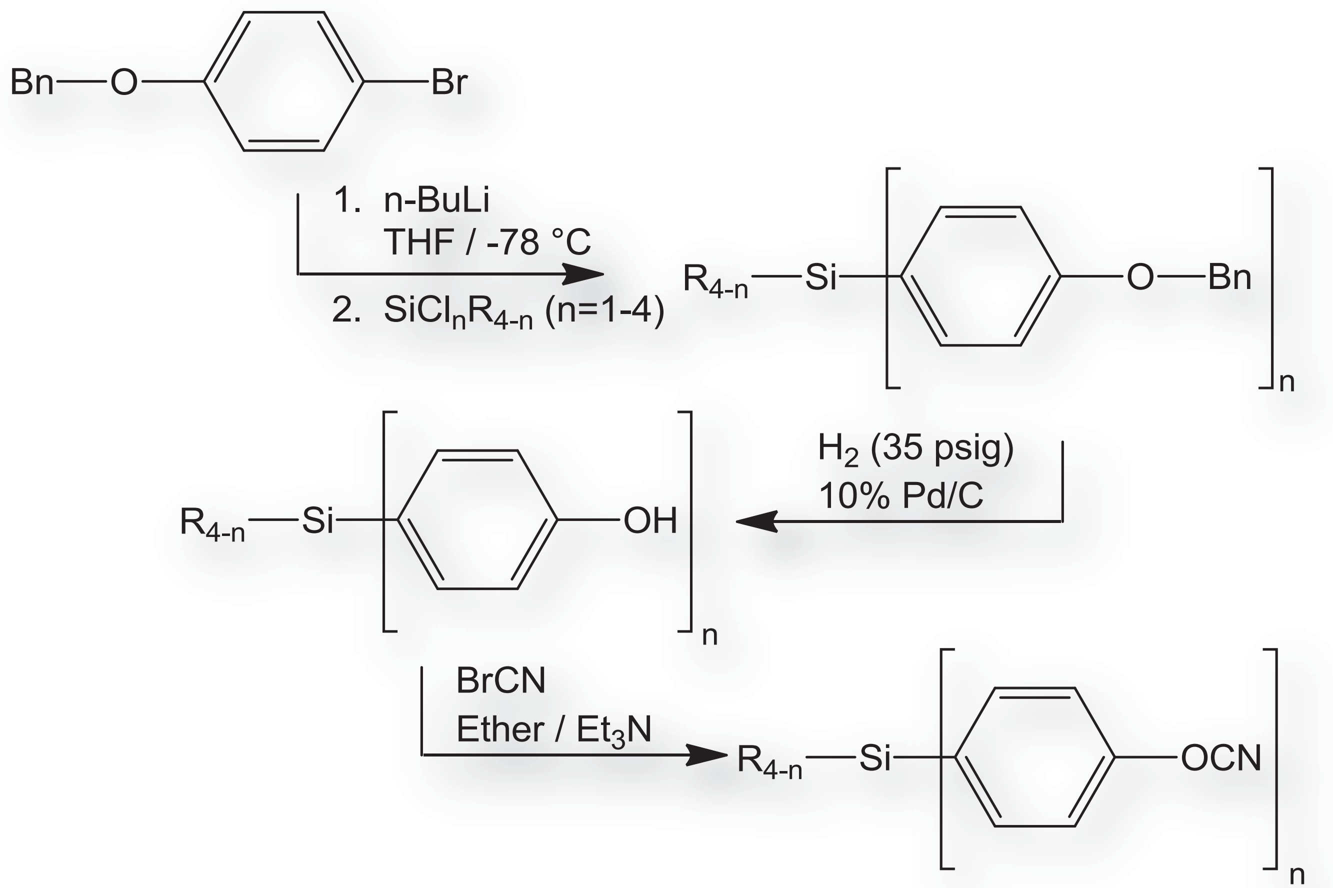


SiMCy

STT3

Catalyzed systems use:
160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol,
All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N_2, cure schedule for 1 hr at 150 °C followed by 24 hrs at 210 °C, with ramp rates at 5 °C / min.

General Synthesis for Si-Containing Monomers



- SiMCy is the n=2 case (Si in network segment), n=3 or n=4 produces Si at network junctions

Si-Containing Cyanate Esters: Crystal / Volumetric Properties

Compound / Property	BADCy	SiMCy	ESR255	STT3
Melting Point, °C (monomer)	83	55	115	118
Heat of fusion (J/g, monomer)	105	93	76	75
Density, g/cc @ 20 °C	1.201	1.171	1.270	1.245
Packing Fraction @ 20 °C	0.620	0.610	0.633	0.626
CTE, ppm / °C @ 150 °C	59	70	60	62

Unless indicated otherwise, properties are for as-cured networks with 85-100% conversion. BADCy and SiMCy cured networks were catalyzed.

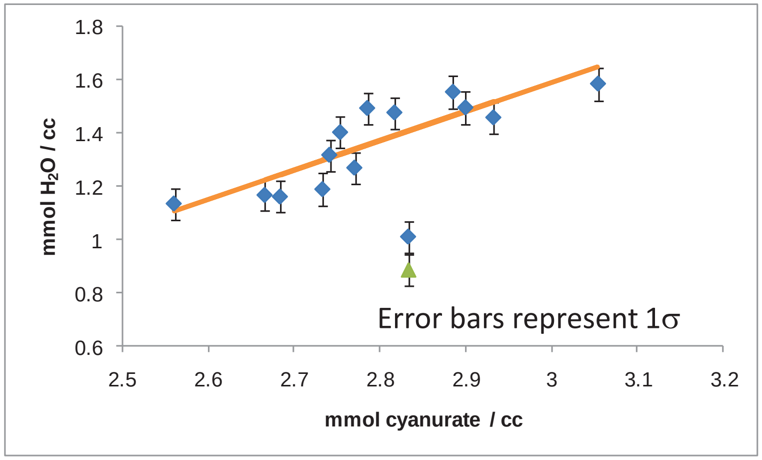
- Incorporation of Si can improve processing characteristics by lowering the melting point of some cyrstalline monomers through packing effects
- Incorporation of Si appears to create free volume and lower network junction density consistently, with a lower fully-cured Tg and higher CTE being the likely result.
- Note that differences in cure can confound these effects to some extent.

Correlation Between Water Uptake and Cyanurate Density

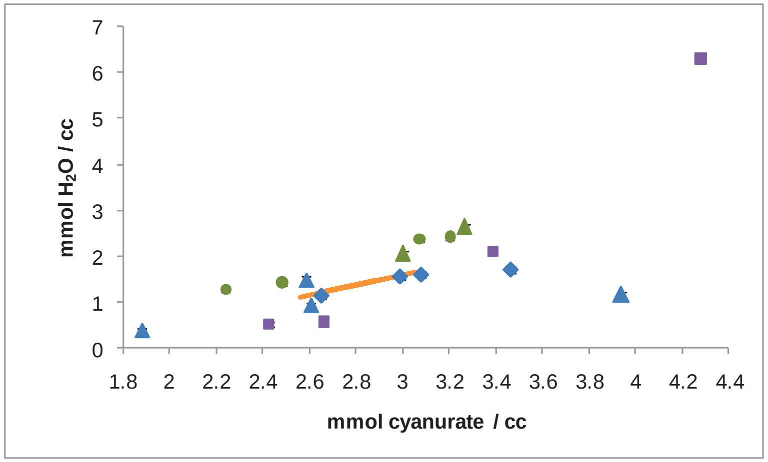
Cyanate Ester - mmol cyanurate/ cc	mmol H_2O / cc
BADCY /2.9	1.7
LECY/ 3.1	1.6
SIMCY / 2.7	1.1
THIOCY / 3.9	1.2
METHYLCY / 2.6	0.9
AroCy F / 2.6	1.5
REX-371 / 3.3	2.6
RTX366 / 1.9	0.4

•Based on data in Appendix a-3 of Hamerton, I (ed)., Chemistry and Technology of Cyanate Ester Resins (Blackie Academic, 1994) (uses monomer density)

In blend samples studied …



… and over all types of CE resins …



Blue = biphenyl
Green = three-arm
Purple = single-ring (meta)
Orange = blend data
Triangle = lit. value (x-axis uncertain)

- Maintaining a low density of cyanurate groups appears to limit water uptake

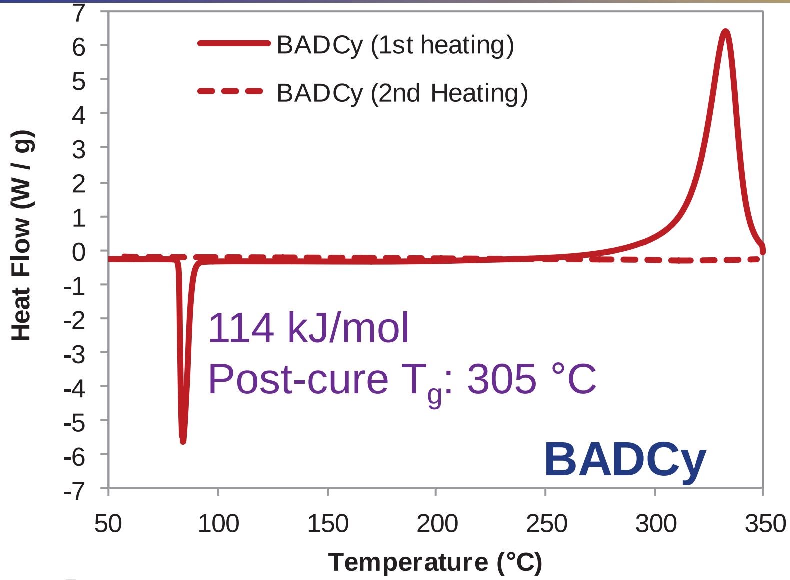
Si-Containing Cyanate Esters: Effect of Exposure to Water

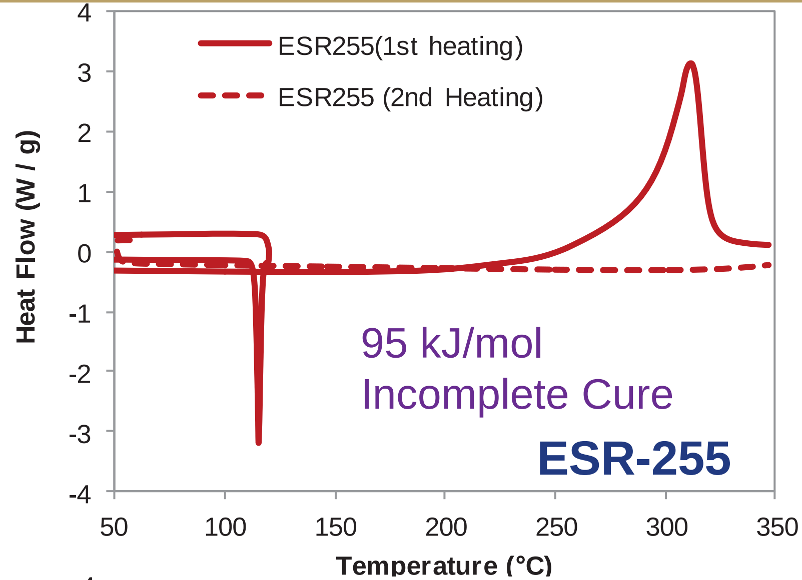
Compound / Property	BADCy	SiMCy	ESR255	STT3
Cyanurate Density at Full Cure (mmol/cc)	2.9	2.7	3.3	3.1
"As Cured" Dry T_G (°C)	278	254	245	>350
"Fully Cured" Dry T_G (°C)	309	266	>420	>350
Water Uptake (96 hrs / 85 °C)	2.3%	1.8%	3.5%	5.5%
"Wet" T_G (°C)	206	186	224	194

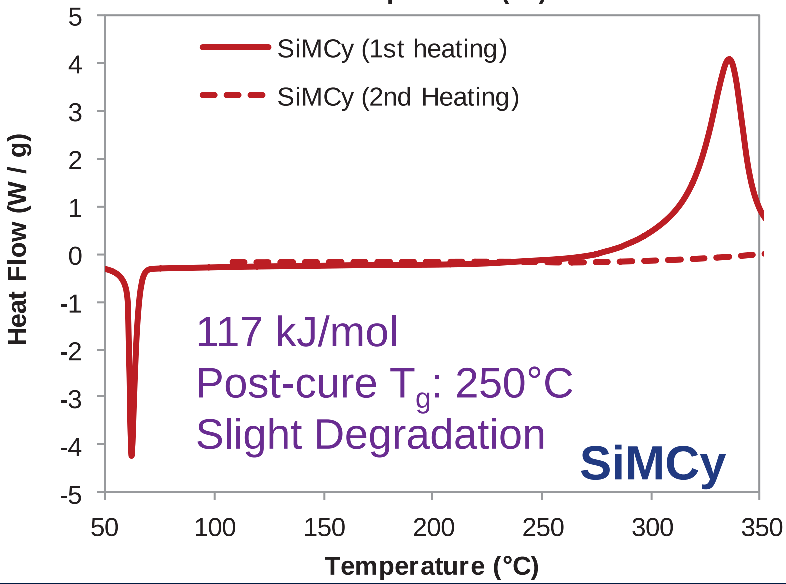
Unless indicated otherwise, properties are for as-cured networks with 85-100% conversion. BADCy and SiMCy cured networks were catalyzed.

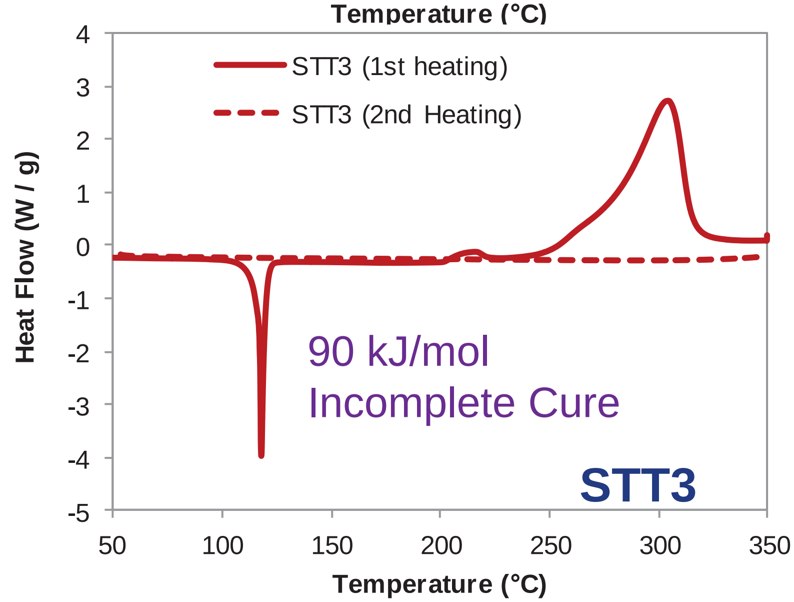
- The lower packing fraction of Si-containing cyanate esters results in fewer cyanurate groups per unit volume, which is expected to lead to reduced water uptake.
- Although water uptake in SiMCy is lower than in BADCy, as expected, for the tricyanate analog, the water uptake is about twice as large as expected.
- The differences in water uptake are not enough to outweigh the differences in segment flexibility in determining the "wet" T_G

Si-Containing Cyanate Esters: Non-isothermal DSC

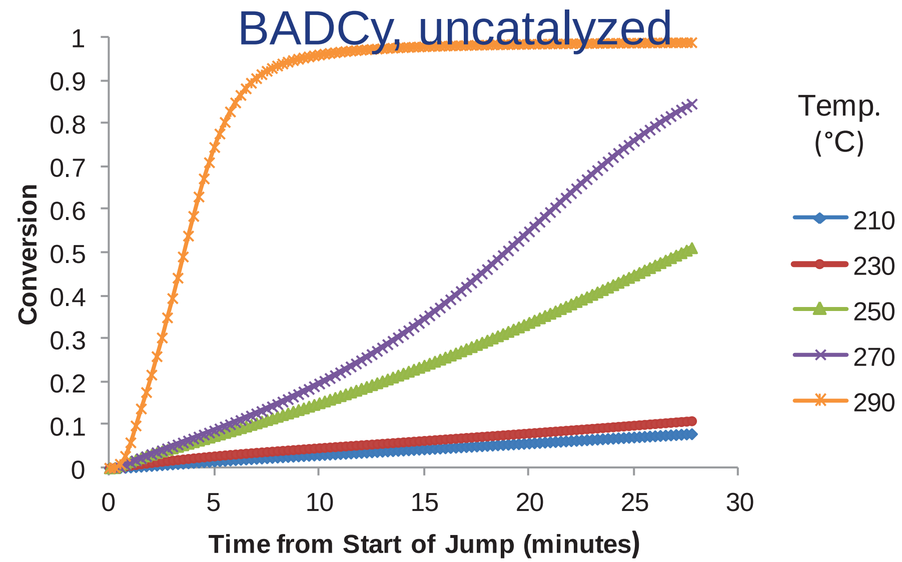


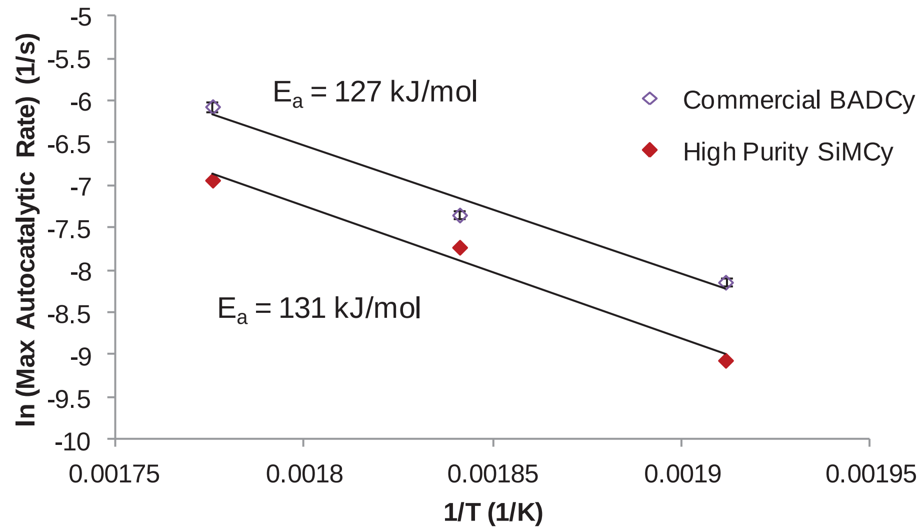


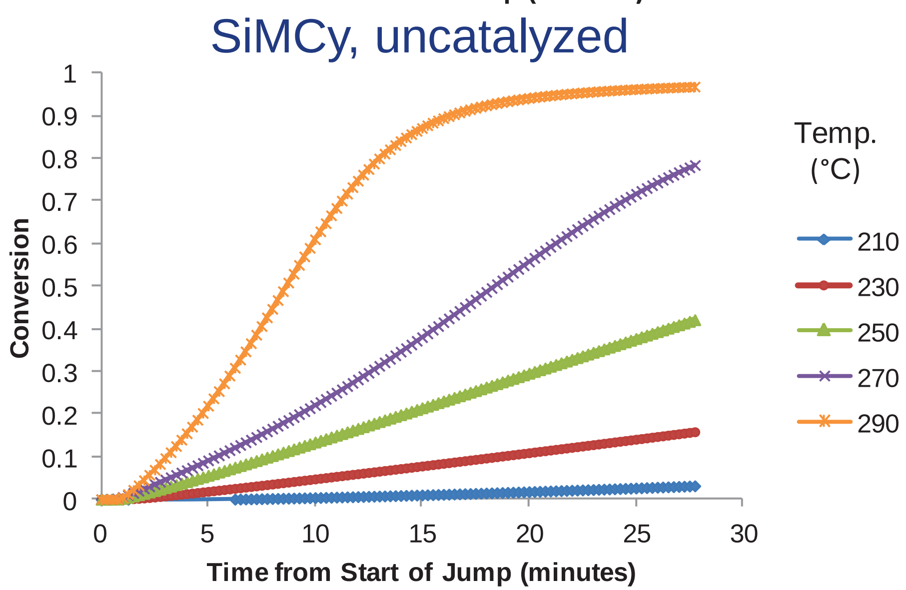




Si-Containing Dicyanates: Cure Kinetics

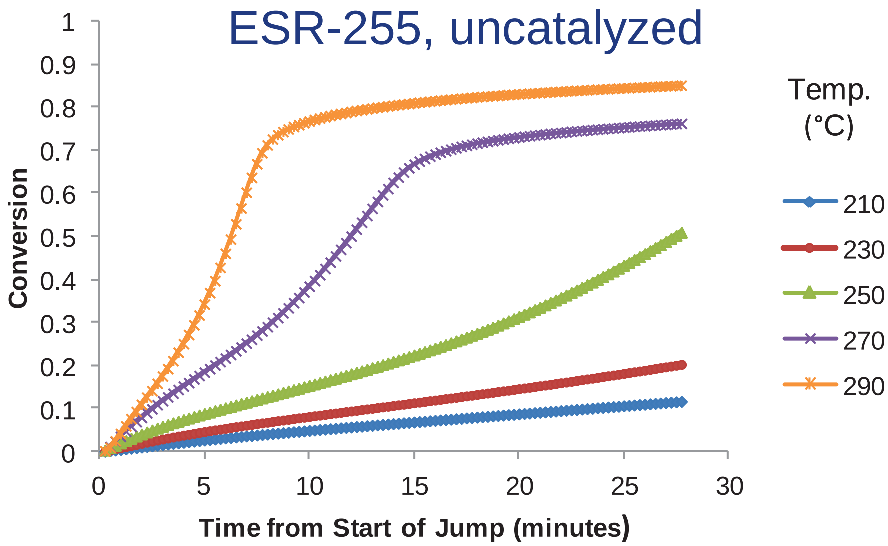


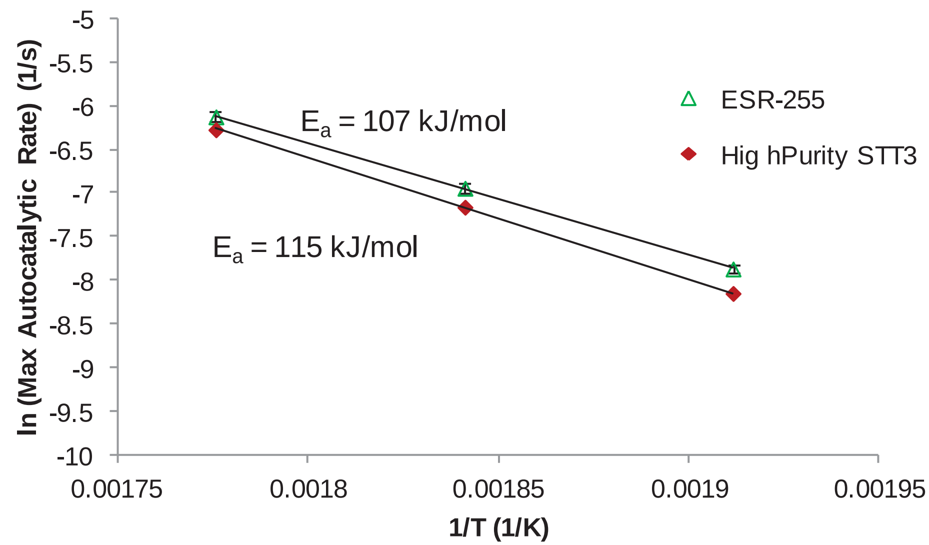


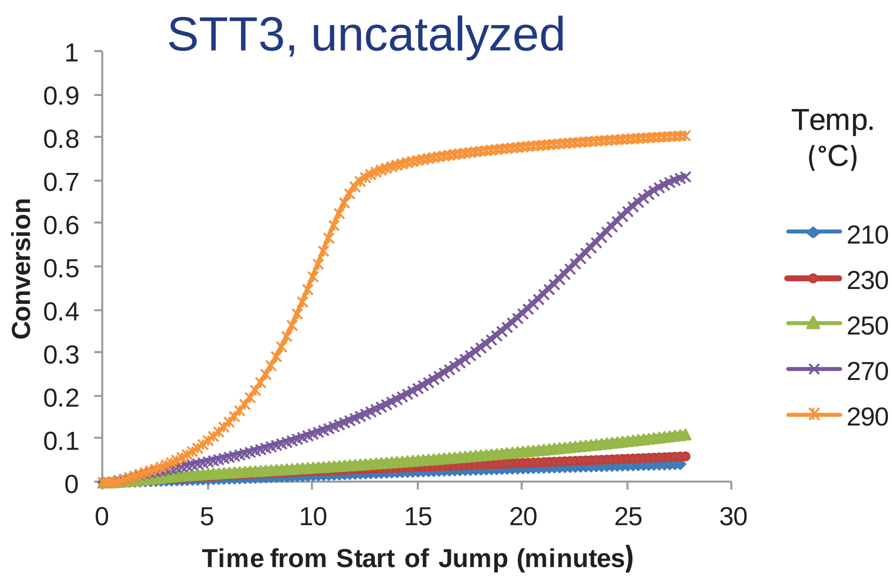


- Although the dependence of cure rate on temperature appears more drastic in BADCy, the most rigorous kinetic-based model data for high purity compounds does not indicate a significant difference in activation energy
- Both BADCy and SiMCy achieve near complete conversion readily

Si-Containing Tricyanates: Cure Kinetics

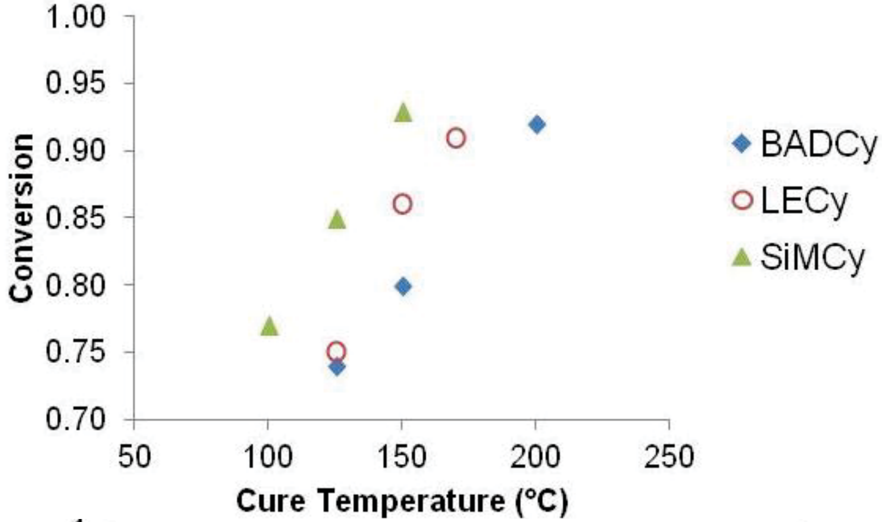


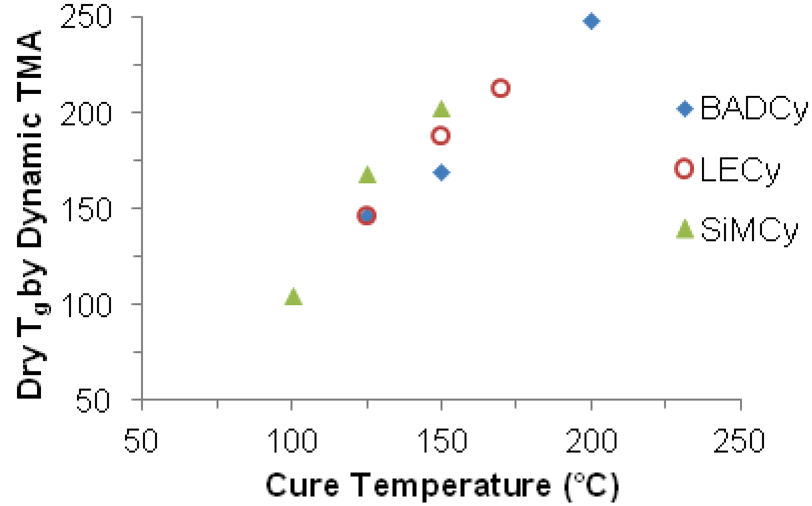


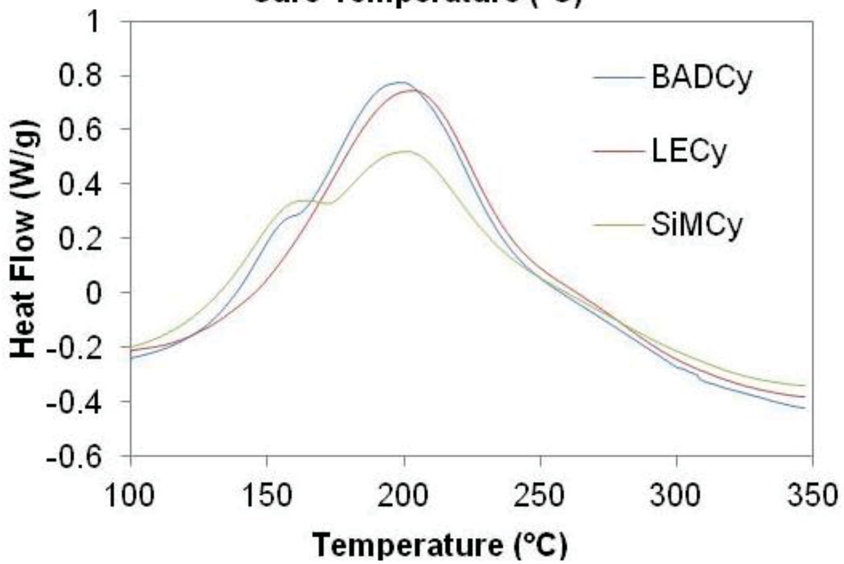


- Like the dicyanates, the tricyanates show no effect of silicon substitution on the auto-catalytic activation energy
- Both ESR-255 and STT3 do not achieve full conversion even when cured at high temperatures, in accord with the shape of the non-isothermal DSC curves

Si-Containing Cyanate Esters Late Stage (Vitreous) Cure



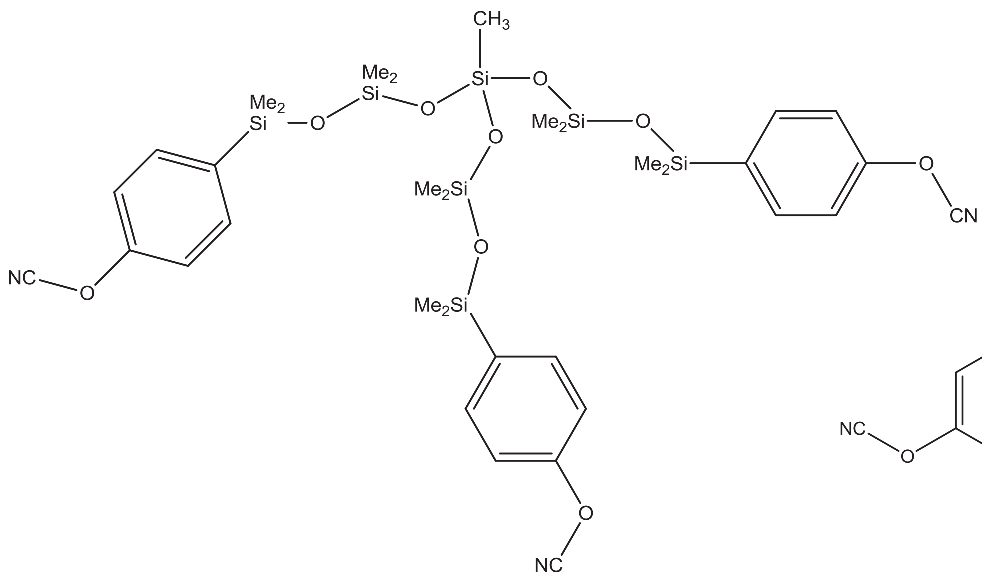




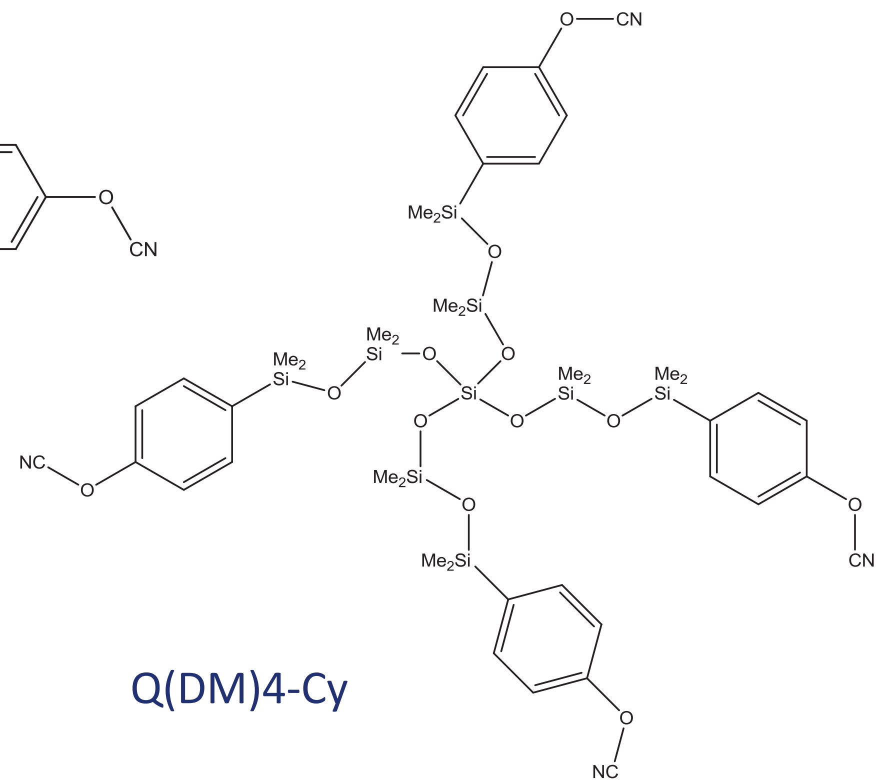
Systems catalyzed with 160 ppm Cu (AcAc) + 2 phr nonylphenol

- SiMCy cures faster and to a greater extent at lower temperatures when catalyzed.
- The relative ease of vitreous cure enables SiMCy to attain a higher T_g for a given cure temperature, despite having the lowest T_g for a given conversion.
- These effects likely caused by flexible core

Siloxane-Containing Cyanate Esters



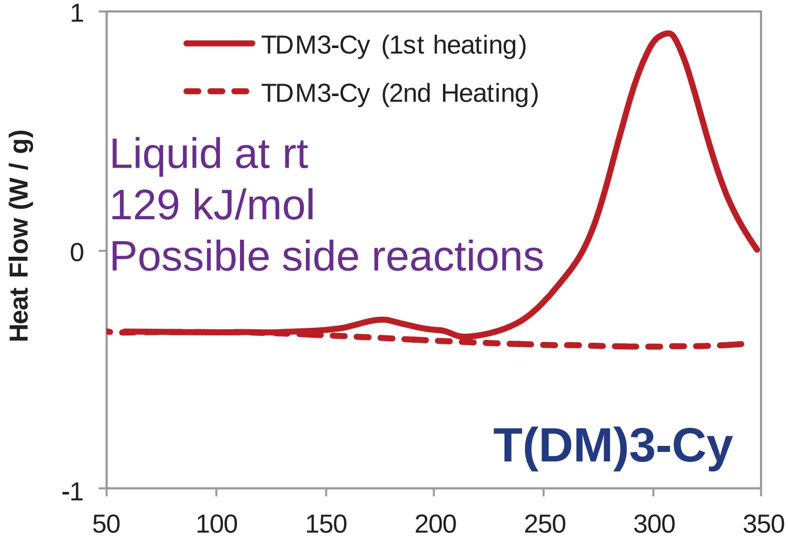
T(DM)3-Cy

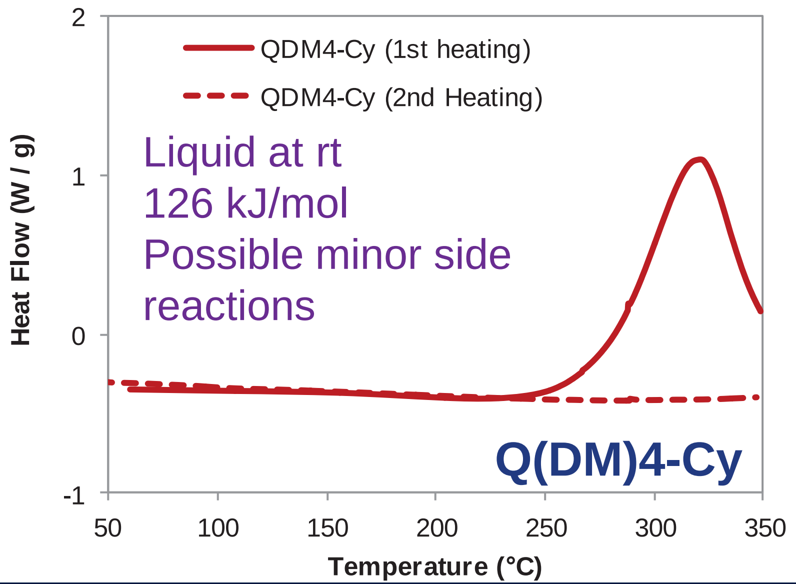


Q(DM)4-Cy

- Higher inorganic content expected to result in better char yields at temperatures over 600 °C
- Balance of siloxane units for flexibility and branch points for elevated glass transition temperature

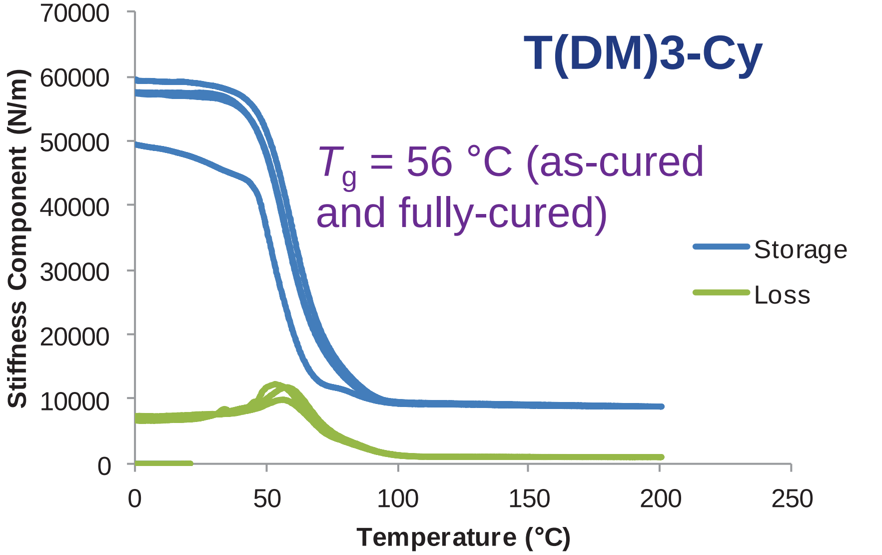
Siloxy-Containing Cyanate Esters: Non-isothermal DSC

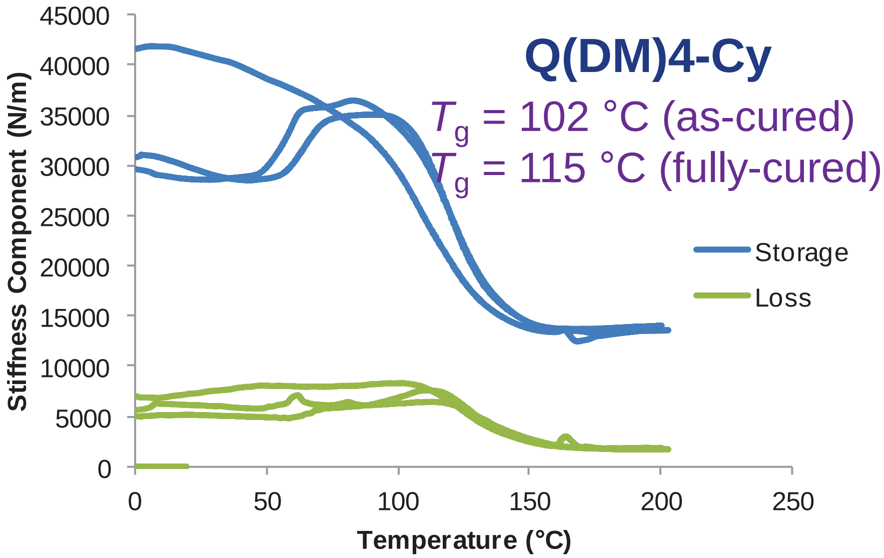




- Exotherm behavior is typical of high purity cyanate ester monomers
- Both monomers are room-temperature liquids and cure to strong solids, DSC indicates a wide processing window
- Enthalpies of cyclotrimerization are typical of highly flexible cyanate esters but may include some heat from minor side reactions
- Symmetrical exotherm shapes are typical of highly flexible cyanate ester monomers; the monomer glass transition temperatures near -70 °C also indicate a high level of segmental flexibility
- Post-cure glass transition temperatures were not readily detected via DSC
- In summary: these are indeed highly flexible, easy to process cyanate ester monomers

Siloxy-Containing Cyanate Esters: Glass Transition Temperature

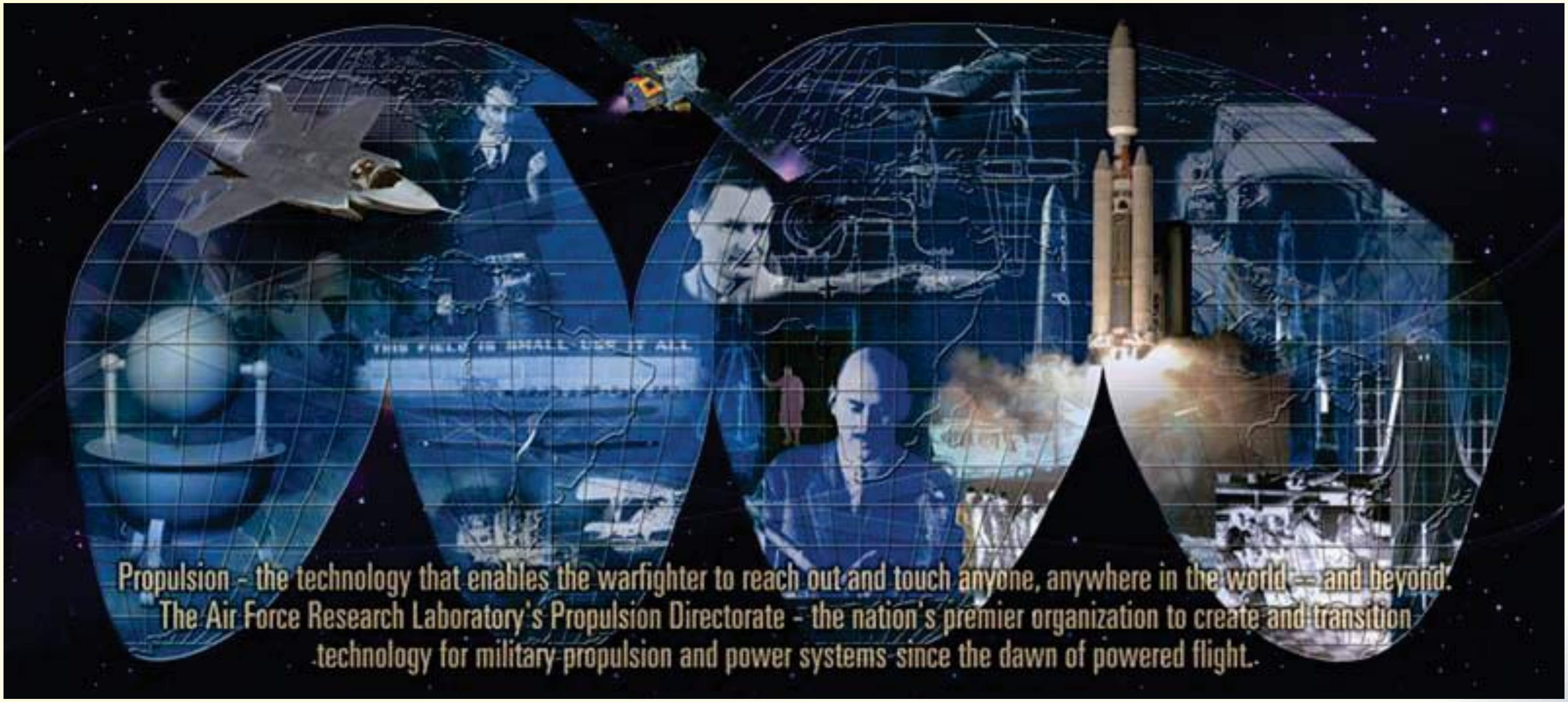




- Both cyanate esters showed a relatively low glass transition temperature for cyanate esters.
- The cyanurate density for these resins is roughly half that of typical cyanate esters.
- The branch point adds some stiffness, but not enough to make up for the long distance between network junctions.
- Further optimization of the cross-link and junction density will be needed to produce cyanate esters with both flexible core regions and high glass transition temperatures.

Summary

- Incorporation of silicon into thermosetting materials provides an important means of improving segment and junction flexibility, in addition to improving thermo-oxidative stability
- It appears that silicon substitution does result in increased free volume, a lower fully cured T_g, and, when compared at the same degree of conversion, lower density, lower packing fraction, and higher coefficient of thermal expansion
- The effect of silicon substitution on properties such as crystal melting point and water uptake appear to depend strongly on the specific architecture used
- As seen in previous studies, the use of siloxane segments in cyanate esters provides for high levels of flexibility and ease of processing. Though branch points may moderate the decrease in T_g, both the cross-link and branch point densities must be carefully optimized to provide both flexibility and a desirable T_g



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